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Review

Recent Advances in the Utilization of Tungsten Residue: A Mini Review of China

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Abstract: As a metal of strategic value, tungsten plays an important part in civil and military applications. Currently, China is the biggest tungsten producer all over the world, and the metallic smelting technologies for tungsten are well established. However, the harmless recovery and treatment procedures for tungsten residue remain rather underdeveloped. The treatment of tungsten residue generally includes the recovery of valuable metals (e.g., scandium, tantalum, and niobium) and the solidification of toxic elements (e.g., arsenic, lead, and chromium), which may control the transfer of these elements and metals. If treated improperly, the resource of tungsten residue may be wasted, and potential environmental risks could arise. Therefore, the safe disposition of tungsten residue has become the limit factor and an urgent problem to be solved for the sustainable development of tungsten-related industries. In this regard, we reviewed the industrial background of tungsten and the composition and toxicity characteristics of tungsten residue. In addition, particular attention was paid to the harmless utilization processes and technologies for tungsten residue, which were then systematically compared in terms of the applicable situations as well as their advantages and shortcomings. Finally, the development trend for the harmless utilization of tungsten residue was discussed, and some proposals for further studies were provided.

Keywords: tungsten residue; utilization; harmless treatment; valuable metal; hydrometallurgy

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1. Introduction

As a rare metal, tungsten has a high melting point and stable chemical properties. In addition, it has excellent mechanical properties at high temperatures, which enable its usage in the production of materials with special properties including hard alloy, strong heat-resistant alloy, and abrasion-resistant alloy [1–4]. Therefore, its role in many fields, such as metallurgy, aerospace, military engineering, electronics, and mechanics, is irreplaceable [5–8]. According to data from USGS, the tungsten reserve across the globe is around 3.5 million tons, which shifted to 3.7 million tons in the year 2021. China has a tungsten reserve of 1.9 million tons, which is more than 50% of the global amount (Figure 1a). Tungsten resources are also found in Russia, Canada, the United States, Vietnam, Bolivia, Spain, and Portugal. Figure 1b shows the distribution of tungsten production across the world in the past 10 years. China is the biggest tungsten producer, with an average annual production of 68 k tons, which accounts for more than 80% of the global production. Vietnam and Russia rank just behind China with percentages of 5–9% and 2–5%, respectively [9–18]. Tungsten mines in China are predominantly located in the provinces of Jiangxi, Hunan, and Hebei, which are the top three across the country in terms of tungsten reserves. Specifically, scheelites ($CaWO_4$) are the main form of tungsten minerals in mines in Northern Jiangxi and Hunan, but in Southern Jiangxi, the most common tungsten ore becomes wolframites ($(Mn,Fe)WO_4$) [19–21]. The potential risk of insufficient global tungsten supply is exacerbated due to the massive need for tungsten as a result of rapid technological development, the continuous consumption of tungsten resources, and higher requirements for environmentally friendly production. Therefore, the status of tungsten as a strategic metal has become ever more significant (Figure 1d) [22].

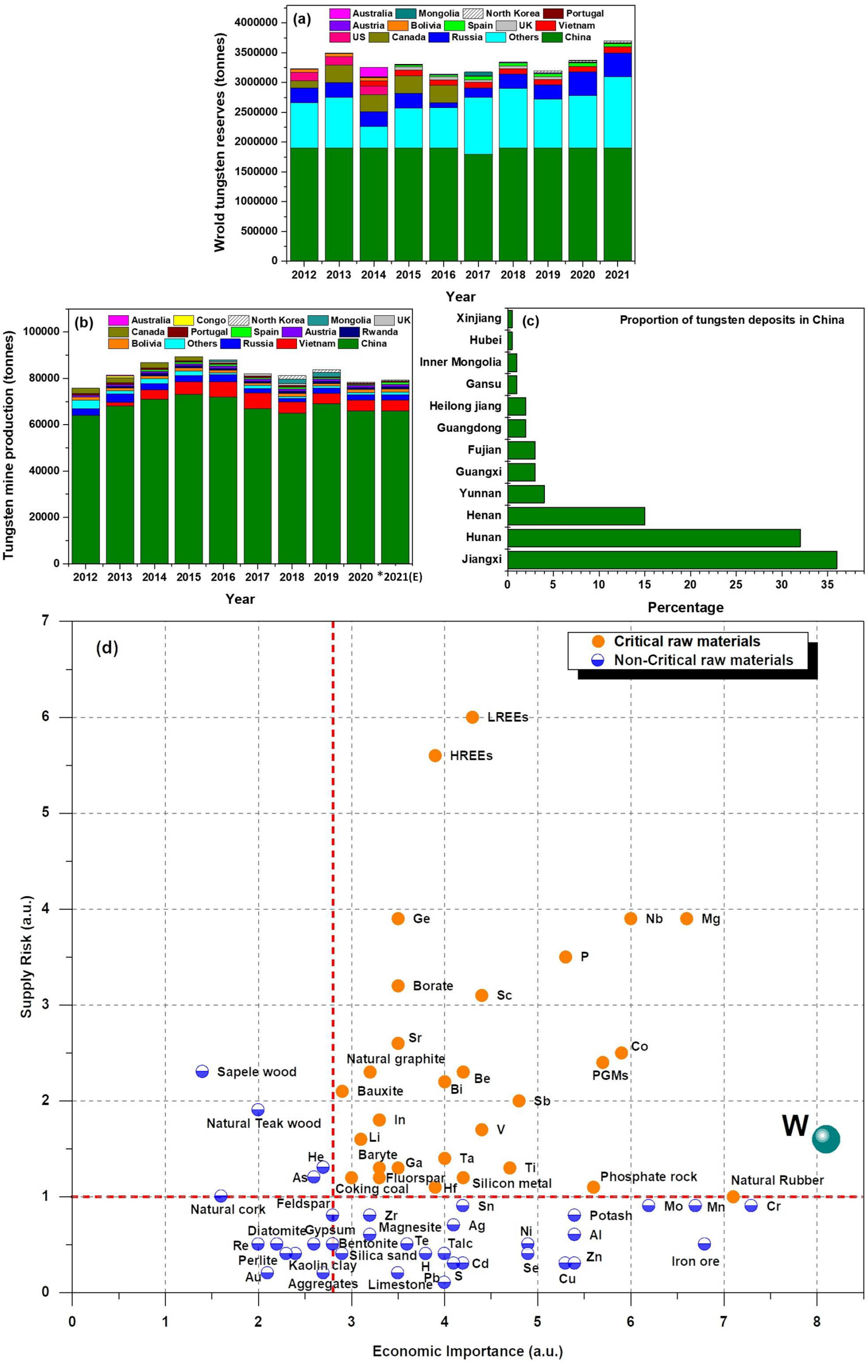

Figure 1. The tungsten reserves (**a**), mine production (**b**) in 2012–2021 in the world (Mineral Commodity Summary, USGS, 2013–2022), proportion of tungsten deposits of China (**c**), and critical raw materials in Europe (**d**) (Study on the EU's list of Critical Raw Materials, 2020). * 2021E; only estimated data for 2021 can be obtained.

The processing procedures vary for raw materials of different compositions. The alkali decomposition procedure, the hydrochloride acid procedure, and the mixed acid (sulfuric acid + phosphoric acid) procedure are three commonly used approaches to obtain tungsten from its ore, and the alkali decomposition procedure is currently the dominant one [7,23–25]. A massive amount of tungsten residue is generated during the smelting of tungsten ore, and the residue coefficient ranges between 0.7 and 0.8. In other words, every 1 ton of ammonium paratungstate (APT) produced from standard tungsten concentrate ore ($WO_3 \geq 65\%$) will be accompanied by 0.7–0.8 tons of tungsten residue. If the tungsten concentrate ore is of lower quality, a higher residue coefficient may apply [26,27]. When obtained via the base-heating procedure, tungsten residue may contain elements such as arsenic, lead, and mercury, which make the residue a potential pollutant for the environment and a waste listed in the National List of Hazardous Wastes (HW48, 323-001-48) [28,29]. However, valuable metals, including tungsten, tantalum, niobium, tin, scandium, and bismuth, which are of high overall utilization value, are also components of tungsten residue [30–32]. Therefore, the concentration and extraction of valuable metals in tungsten residue, as well as the harmless treatment, resource utilization, and pollution prevention of the residue, is of significant importance for the sustainable development of the tungsten industry.

2. Properties of Tungsten Residue

2.1. Composition and Production

The chemical composition of tungsten residue may vary due to the differences in the production procedures and the compositions of raw materials for APT production, but the elemental and phase compositions have certain characteristics. Figure 2 gives a summary of the chemical compositions of several types of tungsten residue, which shows that these complex compositions include dozens of elements (e.g., Fe, Mn, Ca, Si, Na, Al, and W; Figure 2a) and that the main components are Fe, Mn, Ca, and Si (Figure 2b). The contents of these main elements differ across types of tungsten residue, and some types are particularly valuable for recovery because of their rare-metal components such as Ta and Nb. The phase compositions of tungsten residue, as obtained by XRD, vary significantly across different residue types. But, in general, a phase composition includes iron oxides (Fe_2O_3, Fe_3O_4), manganese oxides (Mn_2O_3, Mn_3O_4, MnO_2), calcium oxides (CaO), silicon oxides (SiO_2), and possibly a mixture of several metallic elements (Fe_2SiO_4, $CaSiO_3$, $(Fe,Mn)WO_4$) [33–39]. Thus, the composition characteristics of tungsten residue may be summarized as follows. Firstly, it is composed of predominantly Fe, Mn, Ca, and Si, along with a certain quantity of valuable metals (W, Ta, Nb, Sc, etc.), which make the tungsten residue worthy of recovery. Secondly, toxic elements such as Pb, As, and Cr are also components of tungsten residue, resulting in a high risk of pollution [37,40]. Finally, the phase composition of tungsten residue in which the oxides of Fe, Mn, Ca, and Si are dominant is rather complex.

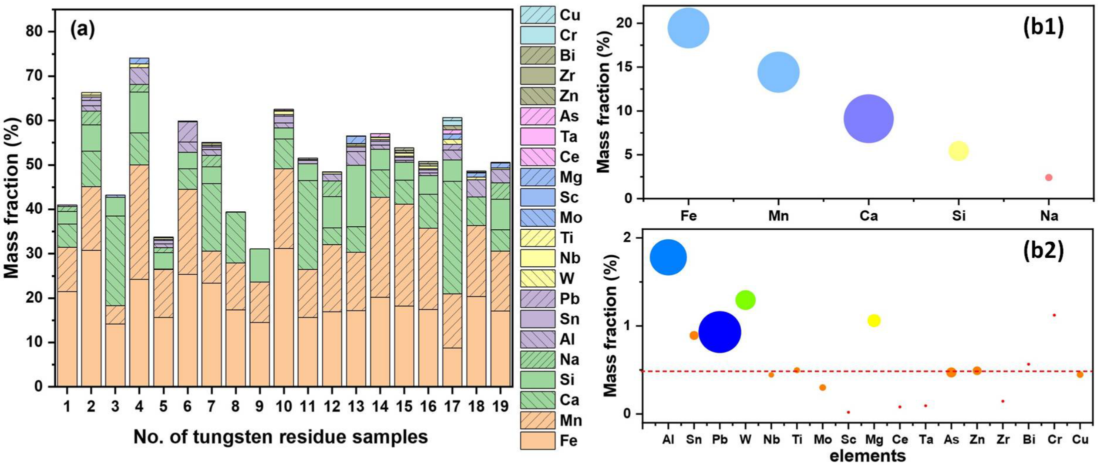

Figure 2. Chemical composition of tungsten residue: (**a**) element contents of some residue samples. Data from [33–39,41–53]; (**b1**,**b2**) average value and fluctuations of element contents in those residue samples, data from: [33–39,41–51].

2.2. Environmental Risks

APT is mainly produced via a decomposition procedure with NaOH. Consequently, tungsten residue obtained from the alkali decomposition procedure has high alkanity and may be categorized as a basic pollutant [37,54]. Yang et al. [29] evaluated the toxicity of tungsten residue obtained from the base-heating treatment of tungsten concentrate ore in 14 APT manufacturers based on the Solid Waste—Extraction Procedure for Leaching Toxicity—Sulphuric Acid & Nitric Acid Method, HJ/T 299-2007 [55] and Identification Standards for Hazardous Wastes—Identification for Extraction Toxicity, GB5085.3-2007 [56]. In the same year, Chen et al. [57] also implemented these methods to investigate the pollution characteristics of tungsten residue in six enterprises that perform the overall recycling of the residue. The main results of these two studies are shown in Figure 3.

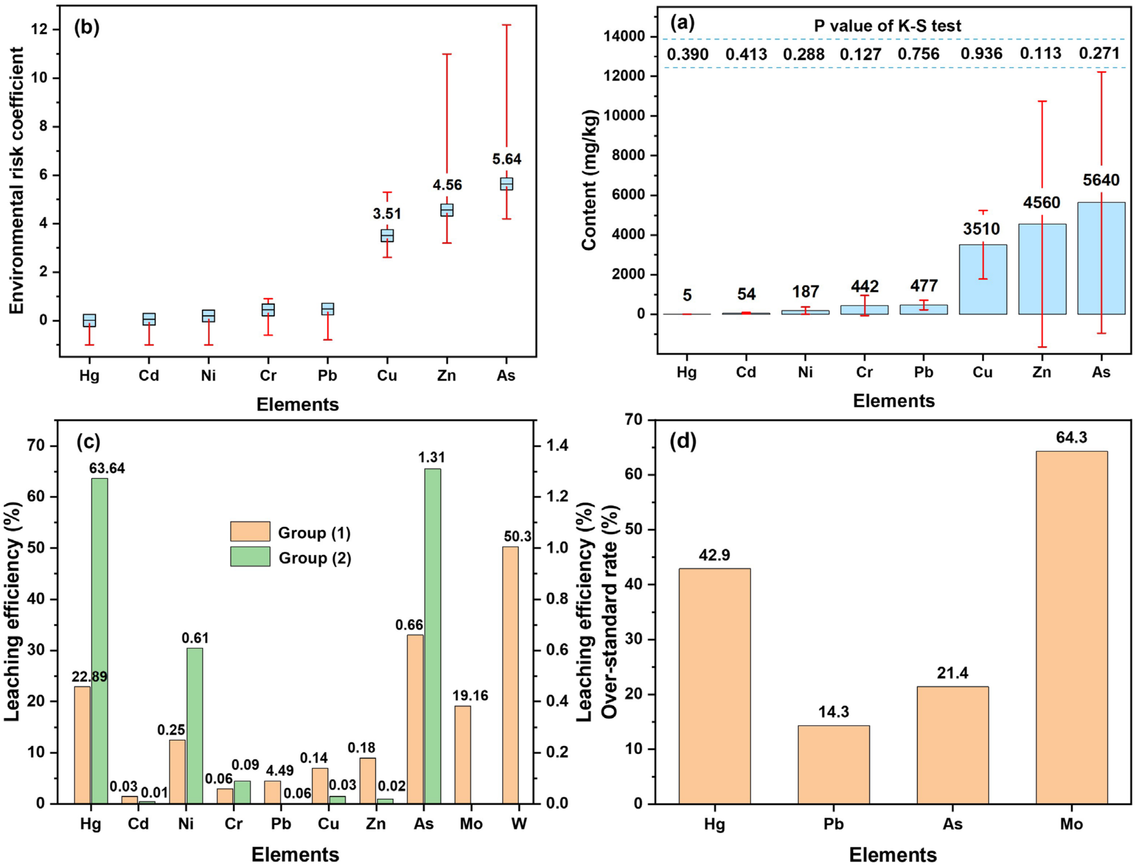

Figure 3. (**a**) Content of heavy metals in tungsten residue (K-S, SPSS test); data from: [29]. (**b**) Environmental risk coefficients of heavy metals in tungsten residue; data from: [29]. (**c**) Leaching efficiencies of heavy metals in tungsten residue provided by HJ/T 299–2007; data from: [29,57]. (**d**) Over-standard rates for Hg, Pb, As, and Mo in tungsten residue; data from: [29].

The Kolmogorov–Smirnov (K–S) test results showed a progressive significance parameter (p value) > 0.05 for all elements investigated, suggesting that the contents of eight heavy metals studied in tungsten residue were normally distributed and statistically significant. More particularly, the average contents of Cu, Zn, and As in the investigated residue samples were 3510 mg/kg, 4560 mg/kg, and 5640 mg/kg, respectively.

Figure 3b shows the environmental risk coefficients of the eight heavy metals (i.e., the ratios of heavy metal concentration to the corresponding limit in GB5085.3-2007). This coefficient is found to be smaller than 1 for Hg, Cd, Ni, Cr, and Pb, indicating small environmental risk for these elements. On the other hand, Cu, Zn, and As have environmental risk coefficients of 3.51, 4.56, and 5.64, respectively, suggesting big environmental risks and the necessity of specific attention being paid to them. Even with these findings, the leaching of toxic elements must be investigated to determine the risk of environmental pollution by heavy metals.

Figure 3c shows the average leaching efficiency of heavy metals from tungsten residue (Group 1: data from Yang et al. [19,29]; Group 2: data from Chen et al. [57]) The differences between the two groups may be attributed to the content and form of presence of each of the heavy metals. Still, generally speaking, Hg, Mo, and W are elements with a high leaching efficiency, and these three elements may easily enter water bodies and present high environmental risks. Moreover, the tungsten residue in the 14 enterprises in Yang et al.'s study demonstrated varying rates of over-standard leaching concentrations for Hg, Pb, As, and Mo compared to the standard requirements, and the over-standard rates (i.e., the percentages of over-standard residues, Figure 3d) are 42.9%, 14.3%, 21.4%, and 64.3% for the four elements, respectively.

These findings suggest that the leaching toxicity of tungsten residues may vary, and such variance is related to the contents and forms of presence of the constituent elements. However, all types of tungsten residue have a certain risk of environmental pollution, and they must be handled and managed as hazardous wastes (note: they have already been enlisted in the National List of Hazardous Wastes). In addition, for tungsten residue, particular attention must be paid to its Hg, Pb, As, and Mo contents.

3. Treatment of Tungsten Residue

Unlike the extraction of tungsten, the fields of the resource utilization and harmless treatment of tungsten residue started late. Even so, enormous efforts have been made until now. In addition, this field has received much attention thanks to the relevant policies and regulations issued due to the properties of tungsten residue as a hazardous waste. For example, the Environmental Protection Tax Law states that starting from 2018, an environmental protection tax is to be charged at a rate of CNY 1000/ton of hazardous waste emitted [58]. As a result, the production of tungsten residue has become an important limitation factor for relevant enterprises. As of today, the treatments of tungsten residue can be summarized in two pathways, namely the recycling of valuable elements (e.g., W, Ta, Nb, and Sc) and the utilization of the residue as a raw material in the production of other goods (e.g., porous ceramics, concrete, and abrasion-resistant materials). However, the harmless treatment of tungsten residue, including its toxicity reduction, remains largely understudied with few relevant reports.

3.1. The Recovery of Valuable Metals

3.1.1. Tungsten

The tungsten (WO_3) content in tungsten residue is 1.5–5%. As the amount of tungsten residue is large, tungsten becomes a valuable component for recycling [27,59,60]. As of today, tungsten may be recycled from tungsten residue via the approaches of hydrometallurgical leaching, roasting, separation, or alloy treatment [30,44,61–66] (Figure 4). Specifically, in the hydrometallurgical leaching approach, tungsten residue is treated with inorganic acids (e.g., HCl, H_2SO_4, or H_3PO_4) so that the tungsten content may enter the solution from which tungsten will be recycled in later steps.

Su et al. [44] tried to leach tungsten residue with 20% HCl under the following conditions: 100 °C, 4 h, a liquid–solid ratio of 3:1, and a 1% addition of additive A (Figure 5a). The extraction rate of tungsten was no less than 86%, and the tungsten concentration in the extraction solution was 3.65 g/L. Following that, the tungsten content in the extraction solution was absorbed by a weak basic negative-ion resin with a large pore size. When the absorption occurred at 35 °C, with pH = 1 and a flow rate of 8 cm/min, the amount of absorbed tungsten could be as high as 102 g per kg of dry resin. Following desorption with NaOH, purification with $MgCl_2$, and concentration and crystallization, the sodium tungstate (Na_2WO_4) product was obtained, which concluded this recycling procedure for tungsten in tungsten residue. Nevertheless, this report did not mention the composition of additive A.

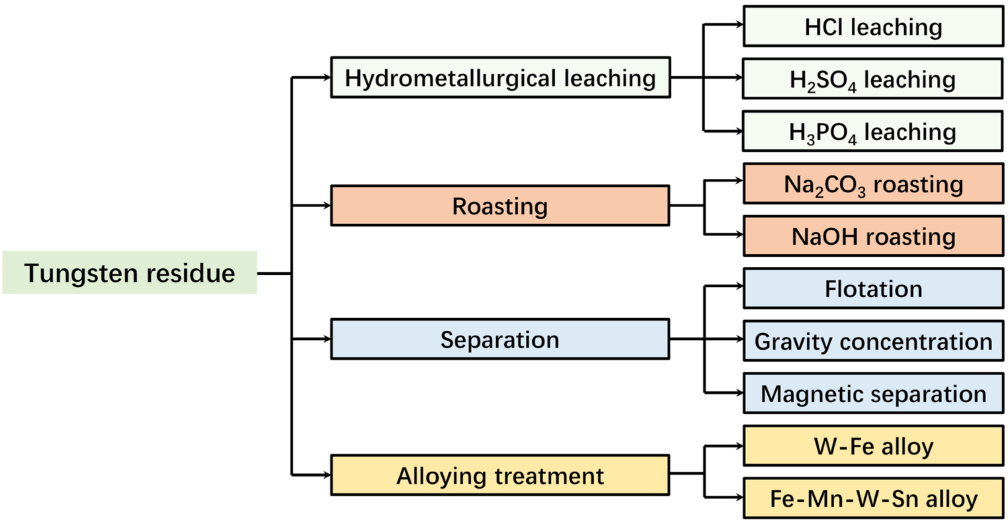

Figure 4. Common methods for the recovery of tungsten in tungsten residue.

Yang et al. [62] recycled tungsten from tungsten residue with a process combining Na_2CO_3 roasting and NaOH leaching (Figure 5(b1)). The residue was firstly roasted with Na_2CO_3 at a mass ratio of 1:0.9 (residue:Na_2CO_3) and 800 °C for 60 min, and the roasted product was subsequently leached at 80 °C for 45 min with 130 g/L NaOH and a liquid:solid ratio of 4. The extraction rate of tungsten was as high as 90.5%, and the overall process was short.

Yang et al. [62] recycled tungsten from tungsten residue with a process combining Na_2CO_3 roasting and water leaching (Figure 5(b2)). When roasted with Na_2CO_3 (5–6 times the theoretical amount), quartz saltpeter, and NaCl (the latter two of which constituted 1–3% of the tungsten residue added) at 800–850 °C and with $CaO/SiO_2 = 2.0–2.5$ for 1.5–2 h, the tungsten residue showed a WO_3 decomposition rate of 88–92%. The roasted product was then leached with water to obtain a solution of Na_2WO_4, which was concentrated to derive NaF crystals and a bulk Na_2WO_4 solution. NaF may be used as a raw material in pressure heating with fluorine salts; the bulk Na_2WO_4 solution was sent to smelting workshops. The WO_3 content in the water-leached tungsten residue was no more than 0.5%. In addition, this process may produce a net profit of CNY 207.9–427.1 per ton of tungsten residue treated (the actual number is dependent on the tungsten content in the residue), which is rather favored in practice.

Luo et al. [63] studied the role of the flotation–beneficiation process in concentrating the valuable metals in tungsten residue (Figure 5c). Mo flotation occurred first when kerosene was added at natural pH. Subsequently, sulfide flotation occurred at pH = 10 with sulfuric acid as the pulp modifier, butyl xanthate as the collector, CMC (0.5 kg/t) as the dispersant, and terpineol as the foamer. Following the removal of sulfides, Bi flotation occurred in the remaining residue with sulfuric acid as the pulp modifier (pH 8–8.8), sodium sulfide (1.25 kg/t) as the sulfurization agent, lead nitrate (250 g/t) as the activator, butyl xanthate as the collector, and terpineol as the foamer. Subsequently, W flotation occurred by adjusting the pulp pH to 8.5. Finally, Sn was concentrated via gravity beneficiation. This process may generate concentrates of Bi, W, and Sn at grades of 8.34%, 13.88%, and 35.39%, respectively. In addition, the end residue of this process is neutral, which may limit its environmental risks.

Huo et al. [64] prepared an Fe-Mn-W-Sn alloy using black and white tungsten residue, heated with base and red mud as the raw materials (Figure 5d). When tungsten residue and red mud were utilized at a mass ratio of 1:1 and the raw materials were treated with 8% reductant at 1550 °C for 120 min, the alloying rates of Fe, Sn, W, Mn, Nb, and Ta were as high as 99.4%, 89.46%, 40.94%, 23.75%, 25.08%, and 17.53%, respectively. In addition, most hazardous elements (e.g., As, Pb, Bi) were reduced and present in soot. This process is capable of simultaneously treating tungsten residue and red mud and recycling valuable metals as alloys.

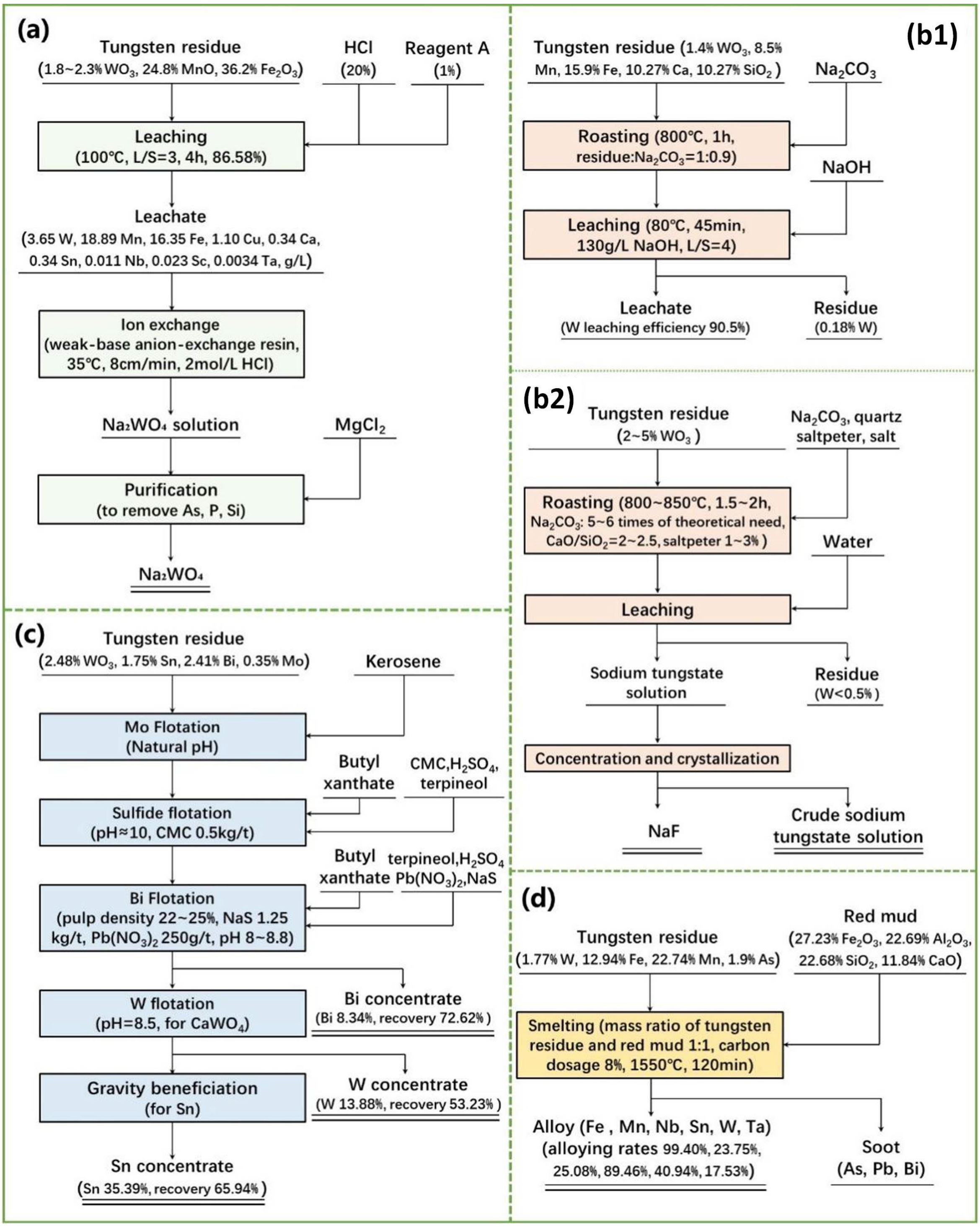

Figure 5. Flow charts for tungsten recovery from tungsten residue. (**a**) HCl leaching; (**b1**,**b2**) roasting; (**c**) beneficiation; (**d**) alloying treatment.

3.1.2. Manganese and Iron

Dai et al. [38] prepared Mn_3O_4 powder from tungsten residue using a process that involves the sulfation roasting, water leaching, purification by precipitation, Mn hydrolysis, and H_2O_2 oxidation of tungsten residue (Figure 6a). The tungsten residue was first roasted with concentrated sulfuric acid overdosed by 150% at 98 °C for 90 min. Following that, the roasted product was leached with water for 120 min, and 88.9% of the Mn contents would be leached in solution while more than 90% of the W and Si contents would reside in the solid residue of the water leaching. A quantity of 10 mol/L NaOH was then added in the leached solution to adjust the pH to around 5. Na2S was added to remove the heavy metal ions, and an appropriate amount of iron powder was added for the reaction at 90 °C for 60 min, which reduced Fe^{3+} into Fe^{2+}. $(NH_4)_2SO_4$ was added in the solution, the solution was boiled until crystallization occurred, and natural cooling was allowed for the system to obtain the sulfuric complex salt crystals. Pure water was used to dissolve the complex salt, and the pH was adjusted to 1–2 using sulfuric acid. Subsequently, H_2O_2 was added to oxidize Fe^{2+} and NaOH was used to control the pH at 6.56 for the reaction at 95 °C for 60 min, which resulted in iron removal. Ammonium solution was added in the iron-free solution to adjust the pH to 8, and Mn was precipitated at 50 °C. H_2O_2 overdosed by 150% was added to the Mn precipitation, and the reaction was allowed to continue for 20 min. Finally, Mn_3O_4 powder was obtained following the filtration and drying of the reaction product.

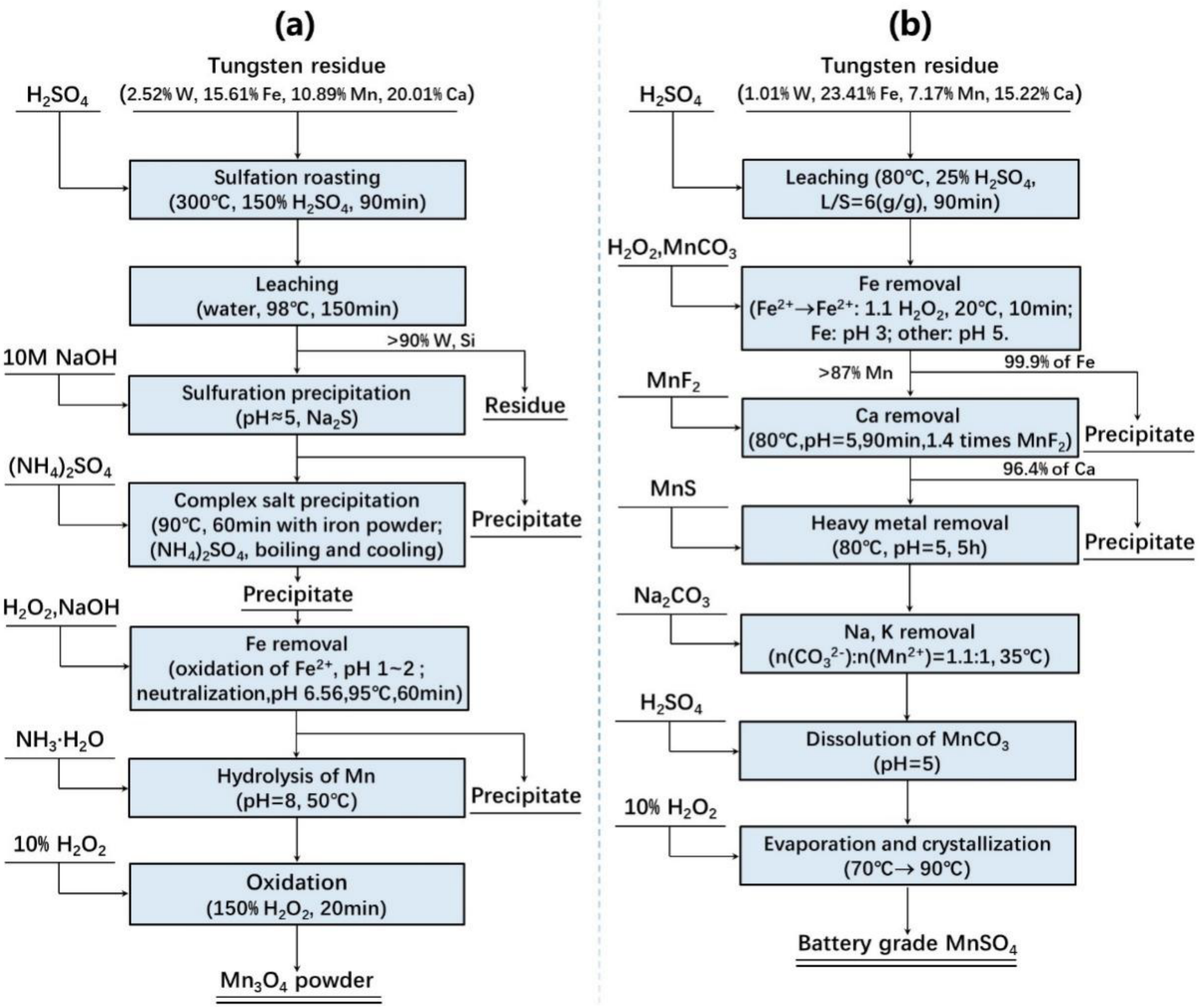

Figure 6. Flow charts describing the process to recover manganese from tungsten residue to form (**a**) Mn_3O_4 and (**b**) to battery grade $MnSO_4$.

Zhang Jianping [67] prepared battery-grade manganese sulfate from tungsten residue (Figure 6b). The preparation started with leaching with sulfuric acid (mass fraction: 25%) at 80 °C and a liquid:solid ratio of 6:1 (g:g) for 60 min. The leaching rates for Fe and Mn were approximately 90% and 81%, respectively. When used at 1.1 times the theoretical amount and 20 °C for 10 min, H_2O_2, the oxidizing agent, may oxidize 99.6% of the ferrous iron contents in such a leached solution. Subsequently, manganese carbonate was added to adjust the pH of the solution to 3 and remove 99.9% of the iron content. The solution pH was then adjusted to 5 using NaOH to remove other impurities, and the manganese content in the solution was 87.16% of the original one. Following that, 96.4% of the calcium content was removed by adding MnF_2 at 1.4 times the theoretical amount in the solution at 80 °C and pH = 5, and the reaction was allowed to proceed for 90 min. Heavy metal ions were precipitated using MnS as the precipitating agent. Next, Na_2CO_3 at 35 °C was added with the ratio of $(n(CO_3{}^{2-}):n(Mn^{2+}) = 1.1:1$ to precipitate manganese and separate Mn from the potassium and sodium contents. Finally, the $MnCO_3$ precipitation was dissolved using sulfuric acid (pH = 5), the solution containing manganese was evaporated at 70 °C until crystallization occurred, and after that, the evaporation operation continued at 90 °C. The crystals obtained were dried at 200 °C to produce the battery-level manganese sulfate.

Fan et al. [68] used an electrolysis-based method to recycle iron from the Fe-W-Sn alloy powder obtained from the high-temperature reduction and smelting of tungsten residue. In the electrolysis setting, the cathode was 316 L stainless steel, and the anode was a lead–calcium alloy bar in a titanium basket uniformly filled with Fe-W-Sn alloy powder. Additionally, the basket had a cover made of polyester fiber with a pore size of 5 μm. Fe elementary substance was prepared at 45 °C, with a pH = 4.5, a current density of 300 A/m^2, and 100 g/L Fe^{2+}; the substance purity was 99.1%, and the current efficiency was greater than 92%. A subsequent four-day experiment showed that Fe obtained from this method had a purity of no less than 97%, with a recovery higher than 92%, and the current efficiency and electricity consumption were approximately 88% and 4757 kW·h, respectively. Moreover, this process was capable of concentrating W and Sn by about three times, and provides new insights for the integrated utilization of tungsten residue.

Based on Fan et al.'s work, Peng et al. [69] made further investigations on the anode (e.g., Fe-W-Sn alloy powder) using electrochemical approaches and revealed the fundamental mechanisms of the separation of Fe from W and Sn from an electrochemical perspective. Tan [70] proposed a process that integrates CO reduction and magnetic separation to recycle Fe and Mn from black tungsten residue. The residue was first reduced at 1000 °C and $CO:CO_2$ = 20 mL/min:180 mL/min for 60 min. The reduction product was ball-milled to control the particle size within 200–400 mesh, and magnetic separation was performed at a magnetic field of 170 mt. The iron concentrate and manganese concentrate had grades of 47.81% and 35.32%, respectively, and the recovery rates of Fe and Mn were 63.32% and 63.65%, respectively.

3.1.3. Scandium

Scandium (Sc) and its compounds have excellent physical and chemical properties, which enable their wide applications in critical fields such as aerospace, nuclear energy, and electronics [71–74]. Therefore, they are indeed strategic resources. The distribution of Sc in the crust is quite scattered, and Sc single ores are very rare. Therefore, low-grade associate minerals and secondary resources are the most common raw materials from which to extract Sc [75–77]. The Sc content in tungsten residue is 0.2–0.4%, and this residue is a very important material from which to obtain Sc [78–80]. Numerous efforts have been made in this regard, and the main steps to extract Sc from tungsten residue include dissolution, separation, and the production of Sc oxides (Figure 7a). Firstly, Sc in tungsten residue is dissolved in solution either by leaching or sulfate roasting–water leaching. The separation of Sc from other elements has been achieved via certain methods such as extraction with a solvent. Further purification has been performed via approaches such as precipitation with oxalic acid, and Sc oxide products may be obtained following calcination [34,45,47,51,78,81].

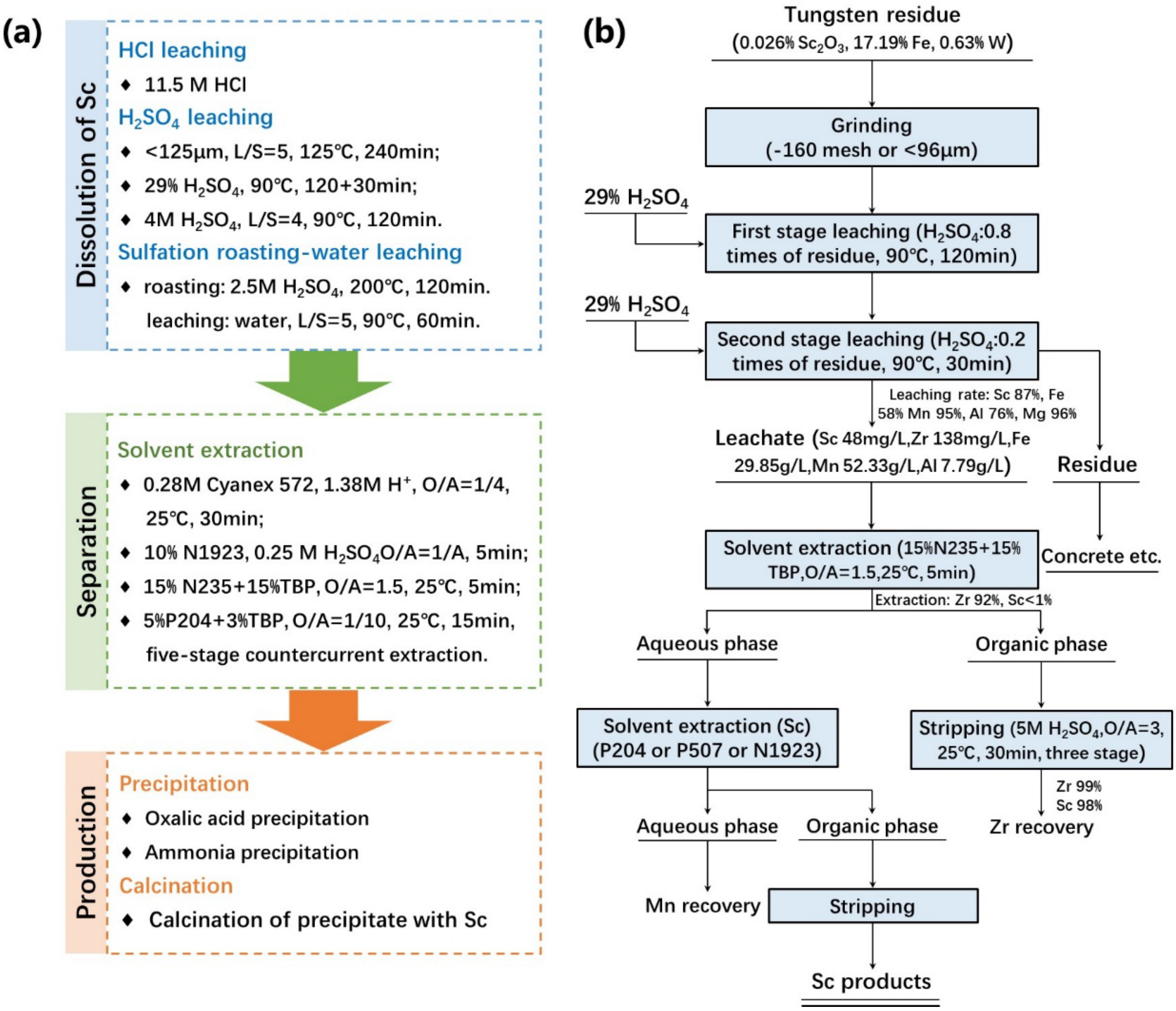

Figure 7. (**a**) General steps of Sc recovery from tungsten residue. (**b**) A typical solvent extraction process for Sc recovery from tungsten residue using H_2SO_4 leaching.

Ding et al. [47,81] used a two-stage leaching with sulfuric acid to recycle Sc from tungsten residue (Figure 7b). The tungsten residue was ball-milled, with its particle size controlled below 96 μm using sieves. A two-stage leaching with sulfuric acid was performed to leach Sc, and the total amount of sulfuric acid was identical to that of the tungsten residue. A quantity of 80% of the total mass of sulfuric acid was added in the first stage (90 °C, 120 min). In the second stage, the remaining 20% of sulfuric acid was mixed with the leached material obtained from the first stage, and the leaching conditions were 90°C for 30 min. In the end, the leaching rates of Sc, Fe, Mn, Mg, and Al were 87%, 58%, 95%, 76%, and 96%, respectively. Specifically, the two-stage approach resulted in an iron-leaching rate of 58%, which was significantly lower than the one obtained from the one-stage method (98%). As a result, the iron concentration in the leached solution decreased markedly, which was beneficial to the co-extraction of iron in the subsequent extraction steps. The extraction was performed first with 15% N235 + 15%TBP + 70% sulphonated kerosene as the organic phase and an O/A ratio of 1.5 at 25 °C for 5 min. This step extracted Zr, and the Zr-containing organic phase was sent to undergo Zr recycling procedures, while Sc remained in the aqueous phase. Sc oxide products could be obtained following the solvent extraction, precipitation, and calcination steps, and the Sc-free solution was set to undergo Mn recycling procedures.

Zhou et al. [34] recycled Sc from the solution obtained from leaching tungsten residue with sulfuric acid using P204 + TBP + sulphonated kerosene as the organic phase for extraction. When the organic phase composition was 5% P204 + 3% TBP, more than 97% of Sc content could be extracted at an O/A ratio of 1/10 and 25°C following a 15 min five-stage countercurrent extraction step. The iron extraction rate in this step was merely 2%, while other impurities remained largely not extracted. Next, a five-stage countercurrent stripping step was performed using 4 mol/L H_2SO_4 at 25 °C and an O/A ratio of 1/1 for 15 min, and in this step, more than 98% of the iron content was extracted and Sc loss was below 1%. The Fe-free organic phase was stripped for Sc using 3 mol/L of NaOH at 50 °C and an O/A ratio of 2/1 for 20 min. The one-stage stripping rate of Sc was higher than 98%. In addition, the bulk Sc products obtained had a purity higher than 82%, with an overall Sc recovery greater than 95%, indicating the efficient recovery of Sc from tungsten residue.

Liu et al. [51] studied the potential application of N1923 to recover Sc from the solution obtained from leaching tungsten residue with sulfuric acid. They used kerosene as the dilution agent and 2-octanol as the modifier. The authors reported a Sc extraction rate of 96.42% for 10% N1923 at 0.25 mol/L of aqueous sulfuric acid and an O/A ratio = 1 following a 5 min extraction step. Following that, the recovered bulk material was washed with a mixture of 7%H_2O_2-10%H_2SO_4-5%HCl% for 3 min. When the O/A ratio was 1 in the washing step, only 2.57% of the recovered Sc was lost, while 96.03% of the titanium and 98.45% of the Fe were removed. Finally, a stripping step was performed on the bulk material (which contained 98% of Sc) with 3.5 mol/L HCl at O/A = 1 for 5 min. Generally speaking, the wet process of leaching with sulfuric acid and extraction with solvents is short in length, simple in operation, and high in Sc recovery. Therefore, it has attracted extensive interest as the primary process to recover Sc from tungsten residue.

3.1.4. Tantalum and Niobium

The abundances of tantalum (Ta) and niobium (Nb) in the crust are as low as 2 ppm and 24 ppm, respectively [82,83]. For Ta-Nb ores to be of value for development, the content of Ta-Nb oxides should be over 0.02% [84,85]. On the other hand, some tungsten residues in China have total contents of Ta-Nb oxides of no less than 0.5%, which makes them favorable raw materials from which to extract Ta and Nb.

Dai et al. [86] concentrated Ta and Nb from tungsten residue using a three-step process consisting of dissolution with a base, water leaching, and leaching with HCl (Figure 8a). Firstly, tungsten residue was mixed with NaOH at a mass ratio of 1:1.2, and the mixture was melted at 800 °C for 80 min. When the melted blocks broke, they were leached with hot water and the solution after leaching was sent to W recycling procedures. The solid residue was leached with two times the theoretical amount of HCl, and Ta and Nb were concentrated in the leached residue, in which the contents of Ta_2O_5 and Nb_2O_5 were 3.47% and 9.13%, respectively. This leached residue could be directly introduced in the production of Ta and Nb, and the recovery of these two metals during the overall concentration procedure was 67.6% (for Ta) an 73.2% (for Nb).

Xiang et al. [87] developed an acid-based approach to recycle Ta and Nb from tungsten residue (Figure 8b). The residue was milled to a particle size of 20 mesh and leached with 6–8% HCl for 5–10 min. This step could remove approximately 70% of the Si content. Subsequently, the remaining residue was leached with a theoretical amount of 22% HCl at 80 °C for 15 min. More than 98% of Fe and Mn components were removed from the residue and entered the leaching solution, which was sent to recycling procedures for Fe and Mn. Most of the Ta and Nb contents were preserved in the leaching residue, and the recovery of Ta and Nb could be as high as 87.4% and 89.2, respectively. Following that, the residue with concentrated Ta and Nb contents was leached with 40% hydrofluoric acid at 1.2 times the theoretical amount and a temperature of no lower than 60°C. The leaching rates for Ta and Nb were more than 92% and more than 98%, respectively. Finally, the leaching solution was concentrated via evaporation, and the vapor could be cooled down to produce high-purity

H_2SiF_6 as a byproduct of the overall process, and this had a total recovery of 80.4% for Ta and 87.4% for Nb.

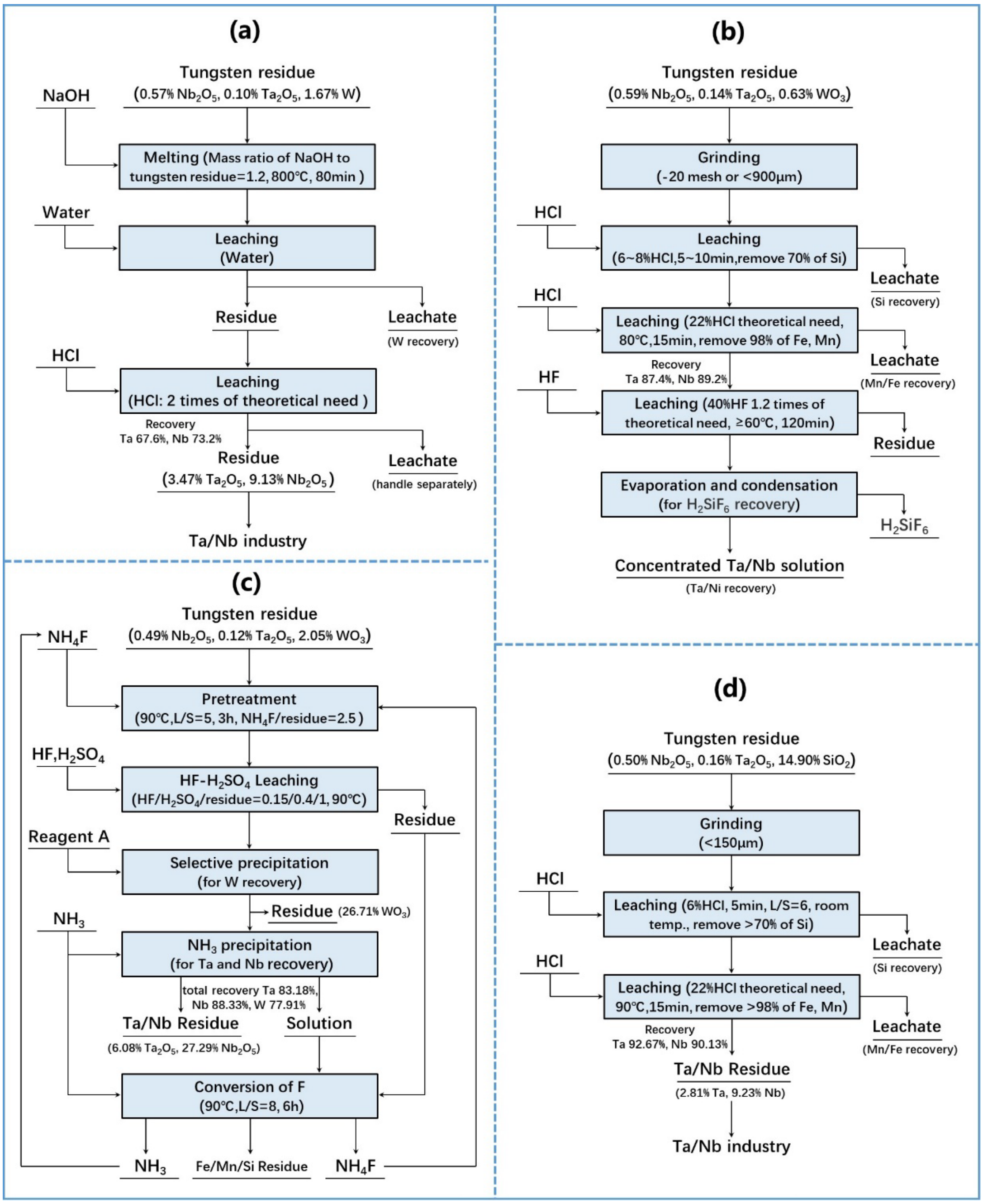

Figure 8. Flow charts describing typical processes to recover Ta and Nb from tungsten residue.(**a**) Three-step process consisting of dissolution with a base, water leaching, and leaching with HCl. (**b**) Acid-based approach. (**c**) Three-step new process based on the solubility differences between the fluoro-ammonium salts of the main impurity elements and metallic fluorides. (**d**) Concentration process using HCl as the primary leaching agent.

Wang et al. [46] proposed a three-step new process to recycle Ta, Nb, and W from tungsten residue based on the solubility differences between the fluoro-ammonium salts of the main impurity elements and metallic fluorides (Figure 8c). Firstly, NH_4F was used as a fluorination agent to transform impurity elements (e.g., Fe, Mn, Al, Si) into their corresponding fluorides. The reactions occurred at 90 °C, a liquid:solid ratio of 5:1, and a mass ratio between NH_4F and tungsten residue of 2.5 for 3 h. Subsequently, the residue obtained from the first step was leached with HF-H_2SO_4 at 90 °C and a mass ratio of HF:H_2SO_4:tungsten residue = 0.15:0.4:1.0 for 2 h. The leaching rates of Ta and W were over 85%, while for Nb, this rate was even higher than 90%. Following the second step, the NH_4F solution obtained from the first step was added back to the leaching pulp at pH = 4–5 along with appropriate amounts of potassium precipitation agents. In this way, impurities like Fe, Mn, Al, and Si would be precipitated as the residue, while Ta, Nb, and W stayed in the solution. After that, tungsten in the leaching solution was selectively recovered via chemical precipitation, and a residue with a WO_3 content of 26.71% was obtained. Following leaching with 5% Na_2CO_3, a solution of Na_2WO_4 could be obtained with a leaching rate of W that was greater than 98%. Ammonium was added to the solution following W precipitation to obtain a precipitation containing 6.08% Ta_2O_5 and 27.29% Nb_2O_5. The overall recovery rates of Ta, Nb, and W were 83.18%, 88.33%, and 77.91%, respectively. The fluorinated residue containing Fe, Mn, Al, Si, and F (at an approximate content of 30%) was mixed with ammonium solution in a sealed reactor at 90 °C and a liquid:solid ratio of 8:1 for 3 h. The leaching rate of F could be more than 88%, and F was transformed into NH_4F for reuse in the first step of the process. This novel process is based on the solubility differences of fluorides and successfully separates the metals to be recycled from the impurities. In addition, the reusability of fluorides makes this process inexpensive in cost, simple in operation, and economical in the technology aspects.

Yang et al. [39] proposed a concentration process for Ta and Nb in tungsten residue using HCl as the primary leaching agent (Figure 8d). The particle size of the tungsten residue raw material was controlled below 150 μm by grinding. Si was leached out using 6% HCl as the leaching agent at ambient temperature and a liquid:solid ratio of 6 for 5 min. This step could remove more than 70% of Si, about 21% of Fe, and around 45% of Mn impurities. Following that, 22% HCl was used at the theoretical amount to leach out more than 98% of the Fe and Mn contents, and the leaching procedure was performed at 80 °C for 15 min. Meanwhile, Ta and Nb were concentrated in the leaching residue with grades of 2.81% and 9.23%, respectively. The overall recovery in this process was 86.57% for Ta and 82.48% for Nb.

3.1.5. Other Metals

Some tungsten residue contains Mo, U, Sn, or Bi, making it valuable for the recovery of these metals important in numerous fields [88–91]. Xiao et al. [42] proposed a wet process to recover W and Mo from tungsten residue based on their process experiments. Specifically, in the first step, concentrated sulfuric acid and 85% phosphoric acid were mixed with tungsten residue at a ratio of sulfuric acid:phosphoric acid:tungsten residue = 63:3.2:100, a liquid:solid ratio of 3:1, and a temperature of 80 °C for 2 h. The leaching rates of W and Mo were 69.7% and 31.6%, respectively. When the mixture ratio became sulfuric acid:sodium chlorate:tungsten residue = 35:10:100, the leaching rates of W and Mo would become 60% and 50%, respectively, given that all other leaching parameters were unchanged. The sulfuric acid–phosphoric acid process was preferred because of its inexpensive cost, but it could only leach W and Mo at a low leaching rate.

Zhong et al. [92] used solvent to extract uranium (U) from a salt solution obtained by leaching tungsten residue (Figure 9a). At a liquid:solid ratio of 3:2, the HCl backflow leaching of tungsten residue for 4 h resulted in a leaching solution containing Mn (73 g/L), Fe (104 g/L), U(VI) (76 mg/L), Th(IV) (63 mg/L), Sc(III) (80 mg/L), Zr(IV) (96 mg/L), Ti(IV) (92 mg/L), and HCl (3.9 mol/L). This solution was extracted using a mixed organic phase of 15% P204 + 10% TBP + 75% sulphonated kerosene for 10 min, and during the extraction, ions of U(VI), Sc(III), Th(IV), Zr(IV), and Ti(IV) entered the organic phase. Subsequently, the organic phase was thoroughly stripped with 4 mol/L hot NaOH at O/A = 4 for 5 min to obtain a composite precipitation of sodium diuranate and hydroxides of other metal elements. The composite precipitation was dissolved in 5 mol/L HCl for the further recovery of U and other valuable elements, and the solution obtained was extracted using 21% N235 + 15% TBP + 64% sulphonated kerosene as the organic phase at O/A = 1, with an initial HCl concentration of 4 mol/L and at ambient temperature for 5 min. The extraction rates of U and Fe were 99.97% and 99.7%, respectively. However, for Mn, Zr, Ti, Th, and Sc, their extraction rates were merely 1.2%, 0.8%, 0.50%, and 0.1%, respectively. Next, the organic phase was washed with 1.0 mol/L HAc at O/A = 1 and ambient temperature for 6 min, which could wash away 99.8% of the Fe and nearly all of the Mn, Zr, Ti, Th, and Sc; meanwhile, the loss of U was merely about 0.2%. The remaining organic phase was then stripped with 1.0 mol/L NH_4HCO_3 at O/A = 1 and ambient temperature for 5 min, and the stripped solution was mixed with concentrated HCl before being boiled. The solution was cooled to 60 °C, and concentrated aqueous ammonium was added in the solution for a 2 h stirring session that produced U precipitation. Finally, the precipitation was dried at 120 °C for 3 h and calcinated at 850 °C for 2 h to obtain U_3O_8 with a purity of 99.75% and an overall U recovery rate of 92%.

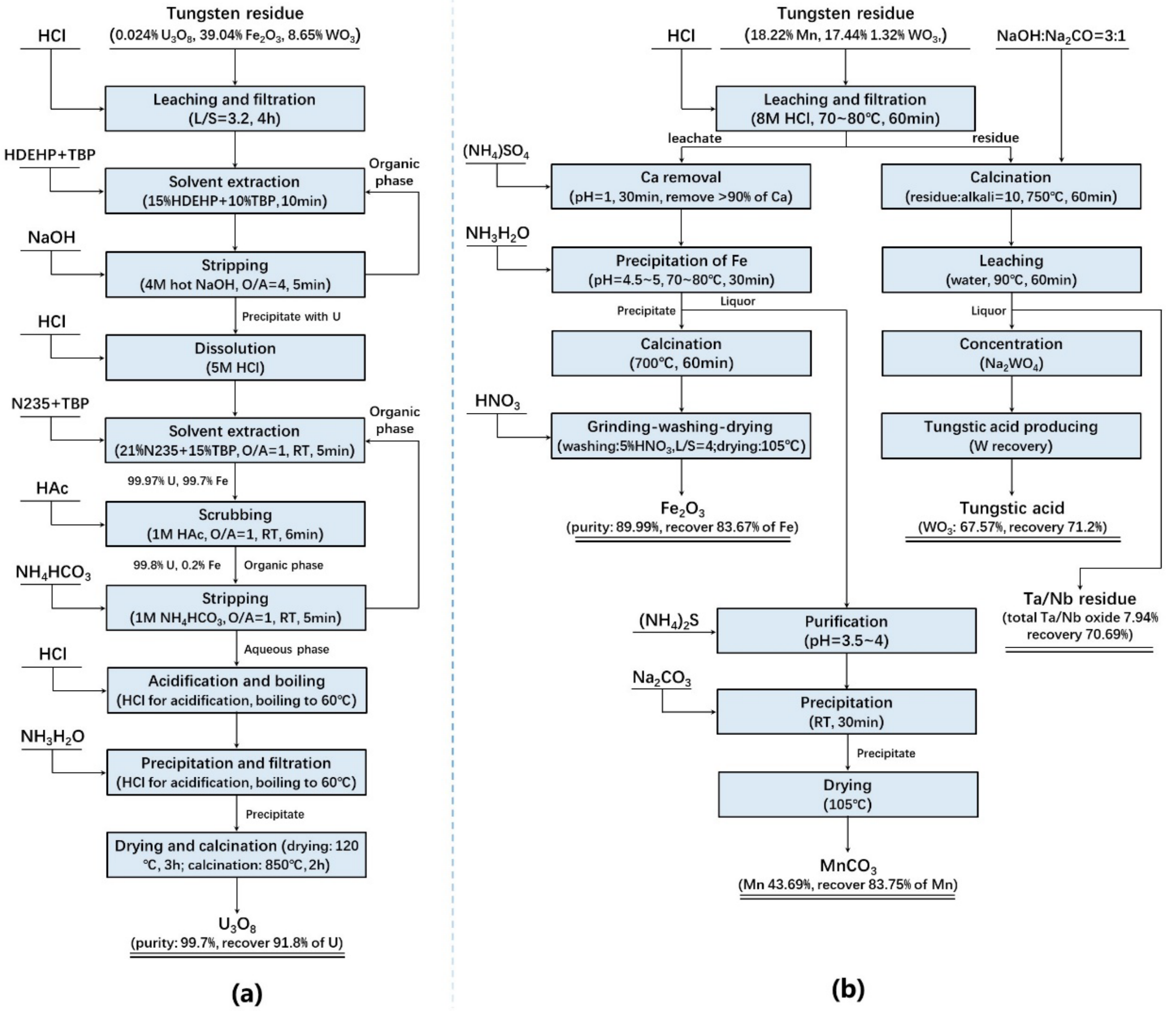

Figure 9. A flowsheet of uranium recovery from tungsten residue (**a**) and a typical flowsheet for the comprehensive recovery of valuable metals from tungsten residue (**b**).

Luo et al. [63] used mineral processing methods to recycle Sn, Bi, and W from tungsten residue. The recovery rates of Sn and Bi in this study were as high as 65.94% and 72.62%, respectively. The detailed process is described in Figure 5c. Liao et al. [48] processed tungsten residue with a reductive smelting process and recycled tin as an alloy with an alloying rate of 67.74%.

Zhong et al. [93] utilized the HDEHP-TBP system to extract and recycle rare earth elements from an acidic leaching solution of tungsten residue. The leaching solution was obtained by leaching the tungsten residue in the study with HCl, whose concentration in the leaching solution was controlled at 3.5–4.0 mol/L. Following that, the leaching solution was extracted with HDEHP to remove Sc, Th, U, Zr, and Ti, then with N235 to get rid of Fe, Zn, and Pb. Subsequently, $MnCO_3$ was added in the extracted solution to adjust the pH to 3.0, and the solution pH was changed to 5.5–6 following the addition of NaOH. This step may have helped remove Al and residual Fe from the system. Following that, the extracted solution was further extracted with 3~4% HDEHP + 4~8% TBP + sulphonated kerosene as the organic phase at O/A = 1/5~1/6 for 15 min. In this step, the extraction rates for rare earth elements, Ca, Cu, Mn, and Mg were around 100%, <10%, 5%, <1%, and <1%, respectively. The organic phase was stripped with 3.0 mol/L hot NaOH at O/A = 5 for 5 min to obtain a precipitation, which was then dissolved with HCl and precipitated with oxalic acid. The precipitation obtained by adding oxalic acid was calcinated at 900 °C for 1 h to obtain the final product (rare earth oxides), and the rare-earth yield was as high as 98.36%.

In fact, the elements recovered, and the recovery methods are based on the chemical composition and phase characteristics of the tungsten residue. A recovery process is required to recover several elements altogether in order to maximize the utilization of resources. For instance, Lai et al. [49] realized the integrated recovery of multiple elements (Mn, W, Ta, Nb, Fe) from tungsten residue via the reasonable designing of the process (Figure 9b).

3.2. Harmless Treatment and Reduction

Scientists have conducted studies on the harmless treatment and reduction of tungsten residue while utilizing the residue as a resource. In other words, their studies aimed to recycle the valuable metals and remove the toxic elements in tungsten residue at the same time, which fit the current ideology of environmental friendliness.

Su et al. treated tungsten residue based on heat reduction with carbon. Reductive smelting was performed at 1450 °C and a mass ratio of SiO_2:Al_2O_3:graphite:tungsten residue = 2:8:15:100. The product was an Fe-W-Mn alloy, with the reduction residue being composed of CaO, Al_2O_3, and SiO_2. More specifically, the reduction residue had no Pb while As and other toxic elements constituted less than 0.1 wt% of the residue, which made the residue appropriate in the preparation of glass ceramics. This process may recycle valuable elements like Fe, W, and Mn while achieving the harmless treatment of smelting residue. However, the authors did not mention the disposition of toxic elements such as As. Xu et al. [94] treated tungsten residue using Na_2CO_3 calcination combined with water leaching. When the mass ratio of Na_2CO_3:tungsten residue was larger than 3:10, the leaching residue obtained from water leaching of the calcination product at 900 °C had an As content of less than 0.1%, with a recovery of W greater than 90%.

Wu et al. [95] proposed a new process to treat tungsten residue as described in Figure 10b. Firstly, tungsten residue was leached using 90 g/L NaOH at a stirring speed of 600 r/min, an oxygen pressure of 0.9 MPa, and 200 °C for 80 min. In this step, more than 97% of As and more than 80% of W were leached in the solution, while the leaching residue had only 0.071 mg/L of As (limit value = 5 mg/L). In addition, the toxicity leaching values of Pb, Zn, Cu, and Hg in the leaching residue were all far lower than the standard ones for hazardous wastes, and so, the leaching residue could be treated as comprising common solid wastes. The leaching solution, on the other hand, was mixed with sulfuric acid to a pH of 2–3 and extracted with Alamine 336. This organic phase specified to extract W was then stripped with 2 mol/L NaOH to obtain a stripping solution, which was subsequently used to prepare sodium tungstate. The organic phase following stripping was reused in the extraction of W. The solution after W extraction was treated with SO_2 to reduce As(V) to As(III), which was then precipitated with Na_2S as As_2S_3. This process can recycle tungsten as sodium tungstate, transform tungsten residue into common solid wastes by leaching with oxygen, and stabilize As into more stable As_2S_3, which is a harmless treatment that utilizes tungsten residue as a resource.

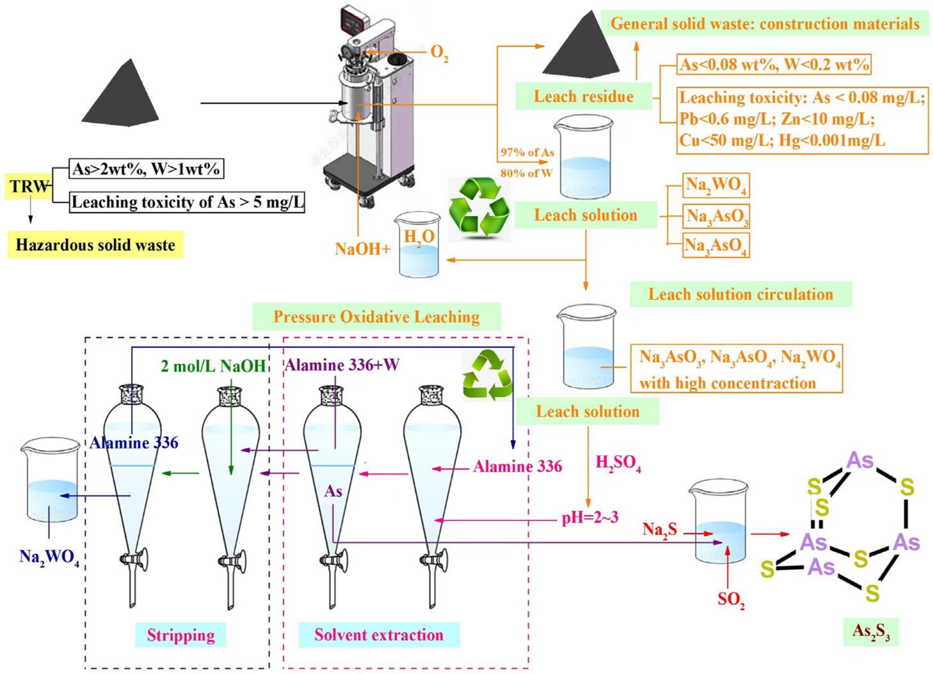

Figure 10. Hydrometallurgical process diagrams for the harmless treatment of tungsten residue. Reprinted with permission from Ref. [95] Copyright 2023 Elsevier.

Fan et al. [36] investigated the potential of acidic decomposition approaches to reduce the amount of tungsten residue and utilize it as a resource. The amount-reduction of tungsten residue was performed using 2 mol/L HCl as the leaching agent at a liquid-solid ratio of 10 and 60 °C for 180 min. This process could increase the W content in the residue from 2.56% to 9.35%, and more than 91% of W was concentrated in the residue. In addition, the amount of residue obtained after this treatment was merely a quarter of the original one. However, the report did not mention the outcome of the leaching solution.

3.3. Preparation of Materials

The utilization of tungsten residue or waste residues obtained following the extraction of valuable elements from tungsten residue as additives in semi-flexible pavements or raw materials for the production of other materials is a possible way to develop these residues as resources [96,97]. However, since tungsten residue is in its essence a hazardous waste, relevant studies are comparably rare.

Jing et al. [98] used diatomite (base matrix), tungsten residue (additive), starch and sodium bicarbonate (composite pore former), and kaolin (sintering agent) to prepare a porous ceramic particle absorption material with a composition of diatomite:tungsten residue:pore former:kaolin = 40%:10%:10%:40%. The mixture of raw materials was held at 500 °C for 30 min and 900 °C for another 30 min before natural cooling, and the porous ceramic absorption material produced had a porosity of 60.67%, a dusting rate of 1.36%, a water absorption rate of 80.45%, and an absorption for ammonia nitrogen of 1.3 mg/g. Jing et al. [33,41] also investigated the absorption performance of porous ceramic particles manufactured from diatomite and tungsten residue for Cu^{2+} and the ammonia nitrogen in the eluviation solution from soil in ionic rare-earth mines. The prepared porous ceramic particles were evaluated for leached toxicity based on HJ/T 299-2007 and GB 5085.3-2007, and they were identified as compliant to the standard requirements. At pH = 5.68 and 30°C, and with an absorption agent amount of 0.5 g, the saturated absorption for ammonia nitrogen was found to be 1.6 mg/g. At pH = 4.5, 30 °C, with an initial Cu^{2+} concentration of 100 mg/L and an absorption agent amount of 0.5 g, the saturated absorption for Cu^{2+} was found to be 9.42 mg/g after 300 min of absorption, and the removal rate of Cu^{2+} was as high as 94.21%.

Ma et al. [50] implemented the technology of high-temperature melting glass transition to transform the toxic components in tungsten residue to safe compounds, thereby reducing the hazard and risk to the environment posed by this residue. In this technology, tungsten residue was mixed with calcium oxide, diatomite, and aluminum oxide and kept at 1500 °C for 0.5–1 h with the base extent of 0.15–0.46. In this way, structurally condensed glassy materials were produced with good continuity, low porosity, and smooth surfaces, meeting the quality requirements of common concrete sand in terms of firmness and crushing value.

Bao et al. [99] investigated the water stability of semi-flexible pavements made from mortar with tungsten residue as the additive. The results showed that when the addition amount of tungsten residue was 15%, the mortar exhibited significant improvements in rupture strength, compressive strength, and stability in water. Nevertheless, despite the fact that this study provided a new possible way for the economical and simple application of tungsten residue, the chemical composition of the residue utilized and the requirements in terms of toxicity for such residue to be used as an additive in mortar were not described.

3.4. Discussion

From the descriptions above, it may be inferred that many approaches can be used to treat tungsten residue, and that these could be roughly divided into hydrometallurgy methods, pyrometallurgy methods, and material preparation methods. Given suitable conditions and the appropriate chemical composition of the residue in question, these methods may utilize the value of tungsten residue to varying extents and be helpful in reducing the amount, toxicity, and environmental risks of this residue. However, some problems, including low recovery, the generation of secondary pollutants, limited processing capacity, and high energy and agent consumption, still wait to be solved.

As of today, research on tungsten residue has been focused on the utilization of the residue as a resource, especially for the recovery of valuable metals. On the other hand, the utilization of the residue as a raw material and its harmless treatment, especially when it comes to the disposition of wastes generated during metal recovery, remain largely underinvestigated. Generally speaking, these techniques have been developed based on the idea of "end treatment", which is the result of tungsten residue accumulation throughout history. In this world, where the environmental crisis aggravates day by day, the tungsten industry must develop in an economical, green, and sustainable way to meet stricter environmental protection requirements.

Therefore, scientists should pay some attention to the source of environmental risks and study the control of pollutants and toxic elements during tungsten smelting so that these substances enter the smelting process in a naturally stable form in smaller amounts. Still, this goal is far from achievable, and scholars are limited to studying tungsten residue through categories. Particularly, one category could be the disposition of such residue via end-treatment approaches, and scholars may develop economical, green, and feasible disposition methods that utilize the residue's value to the maximum extent while not emitting waste. Further studies may try to initiate residue control during the tungsten smelting process, or even during the initial stage of ore mining and frustrating, via process modification and development. Certainly, cost effectiveness will be a significant challenge for the development of new processes, as it should be able to control the environmental risk while minimizing both the energy and agent consumption as well as equipment investments.

4. Conclusions and Prospect

Being composed of several valuable metals (W, Fe, Mn, Ta, Nb, Sc), tungsten residue is an important secondary resource. However, it also contains toxic elements such as As and Pb, and this brings significant value to its harmless treatment, reduction, and utilization as a resource. Decades of investigation have seen rapid development of and significant outcomes for tungsten residue-related treatment techniques in China, but the highly efficient, clean, and economical treatment of the residue remains challenging due to the residue's complex chemical composition and the numerous forms of the relevant elements it contains.

The relevant investigations are largely insufficient in terms of the disposition and management of secondary wastes generated during the metal recovery processes used on tungsten residue, especially in the behavior of harmful elements, element distributions in the three phases and the forms of presence, and the toxicity evaluation of secondary solid wastes. When processed with different approaches, the wastes generated from tungsten residue and the behaviors of harmful elements should vary.

Future treatments of tungsten residue may include a selection and combination of methods based on the characteristics of the residue to be processed, thereby enabling the economical and green disposition of tungsten residue. Meanwhile, more efforts should be made in the development of products with high added values that are manufactured from tungsten residues so as to boost the relevant interest in the industry. In addition, the ideology of end-treatment should be switched to an idea in which pollution management starts in the beginning. The academic field may work on controlling the entry and transfer of toxic elements during tungsten-related processes so as to essentially reduce the amount of toxic tungsten residue. Finally, government authorities could optimize the relevant policies and regulations and support scientific studies in this field to enhance the tungsten-related industry in a sustainable manner.

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